

Behavior of Acrylic Acid–Itaconic Acid Hydrogels in Swelling, Shrinking, and Uptakes of Some Metal Ions from Aqueous Solution

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ABSTRACT: An experimental research of the absorption properties of metal ions onto synthetic hydrogel obtained by solution polymerization of acrylic acid and itaconic acid in presence of *N,N'*-methylenebisacrylamide as crosslinking agent was carried out. The swelling behavior in aqueous salt solutions was studied as a function of divalent cation concentration (Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+}) in

the external solution ranging from 10^{-5} to 1M , at 25°C . The ability of these hydrogels to bind cations was measured at different pH values and metal ion concentrations. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 530–536, 2003

Key words: hydrogels; swelling; metal ions; polyelectrolytes; solution polymerization

INTRODUCTION

Hydrogels are water-swallowable, three-dimensional polymeric networks that have been attracting much attention as functional polymers that possess properties of water absorption.^{1–3} Hydrogels have been the focus of a number of investigations, especially in the last 30 years, because of their considerable applications in many areas.⁴ They can be used as biomedical materials,^{5–8} in the field of medicine and pharmacy, biotechnology, and agriculture, for example.^{9,10}

Polyelectrolyte gels are formed from crosslinking flexible polymer chains to which ionizable groups are attached. These ionizable groups will completely or partially dissociate in solution to form strong or weak electrolyte groups along its chains. These charged groups produce an electrostatic repulsion force among themselves, which will enhance the expansion of the gel network.^{11,12} In an anionic polymeric network containing carboxylic acid groups, ionization takes place as the pH of the external swelling medium increases above the pK of the ionizable moiety. The polymeric network becomes more hydrophilic as the degree of ionization increases.¹³

Thus the swelling of a polyelectrolyte hydrogel in a metal aqueous solution, followed by metal complexation, can be applied to the treatment of diluted aqueous effluents, to recover precious metal, to remove toxic or radioactive elements from various effluents, and to preconcentrate metal for environmental sample analysis.^{14–17} The present study, which deals with the extraction of some metal ions with a poly(acrylic acid–itaconic acid) hydrogel, illustrates these applications.

EXPERIMENTAL

Acrylic acid (Fluka, Buchs, Switzerland) and itaconic acid (Merck, Darmstadt, Germany) were used as monomers. *N,N'*-Methylenebisacrylamide (Aldrich Chemical, Milwaukee, WI) was employed as crosslinking agent and 2,2'-azobis(2-amidinopropane) dihydrochloride (V50; Wako Pure Chemicals, Osaka, Japan) as initiator.

Aqueous solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, and $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ salts were used variously as solvents in swelling and sorption experiments.

Preparation of hydrogels

Hydrogels were prepared by radical copolymerization of acrylic acid (AA) and itaconic acid (IA), at 60°C , for 4 h in nitrogen atmosphere, in cylindrical glass tubes. Total monomer concentration in the reaction solution (water) was 25% (2.5 g) in weight. The initiator and crosslinking agent concentrations were 0.1 and 1 wt %, respectively.

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respectively, with respect to the monomers. All solutions were degassed before polymerization.

The resultant hydrogels were cut into cylinders and washed in distilled water for removal of the unreacted monomers. They were initially dried in air at room temperature and then under vacuum, at 50°C, until constant weight was reached. The dimensions (~ 9 mm diameter, 1 mm thick) were determined using a micrometer.

Swelling in aqueous salt solution

Swelling studies were performed gravimetrically. Xerogel samples were swollen in aqueous salt solutions to equilibrium, in a thermostatic vessel, with constant stirring at 25°C, to determine the hydration equilibrium degree H_∞ . The percentage degree of hydration can be expressed as

$$H = \left(\frac{m - m_0}{m} \right) \times 100 \quad (1)$$

where m is the mass of the wet sample at time t and m_0 is the weight of the dry sample.

Metal extraction and analytical procedure

Absorption experiments were carried out by placing about 0.1 g of poly(acrylic acid-co-itaconic acid) (80 : 20) xerogel into 50 mL of different concentrations of metal salt solutions with constant stirring. Aliquots from the resultant solutions were withdrawn and analyzed, after suitable dilution, by atomic absorption using a Perkin-Elmer 560 spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT).

The dependency of metal uptake on pH and salt concentration of external solution was studied at pH values of 4, 5, and 7. Metal absorption was monitored with a digital pH meter using a glass reference electrode. Uptakes of metal ions onto hydrogel systems can be calculated from the following relation:

$$\text{mg } M^{2+} / \text{g}_{\text{xerogel}} = \frac{C_i - C}{m} V_t \quad (2)$$

where C_i and C are the initial and the equilibrium concentrations of metal ions in mg L^{-1} , V_t is the total volume of metal solutions in liters, and m is the mass of the dry polymer in grams.

Desorption experiments were carried out with the hydrogel loaded with $10^{-3} M$ metal ion concentration. The hydrogel was put into contact with 50 mL of different acid solutions at different concentrations. The mixture was stirred for 2 h. The hydrogel was separated and the metals were analyzed in the solution as previous described. The percentage of metal

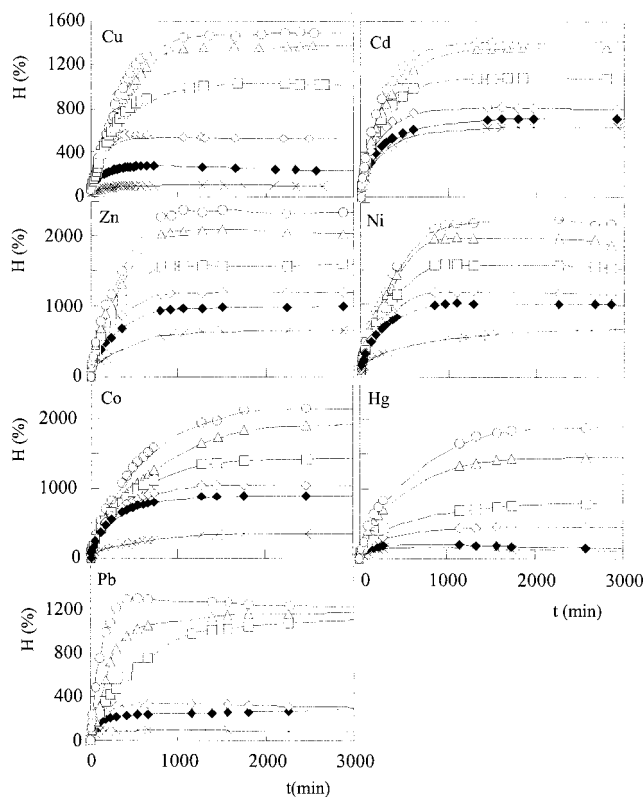


Figure 1 Dynamic swelling curves of AA/IA hydrogels with different concentrations of metal ion: (○) $10^{-5} M$; (△) $10^{-4} M$; (□) $10^{-3} M$; (◇) $10^{-2} M$; (◆) $10^{-1} M$; (×) $1M$.

eluted was calculated by comparing the amount of metal initially loading the hydrogel and the amount of metal in the final supernatant.

RESULTS AND DISCUSSION

Hydrogel swelling in salt solutions

The dynamic swelling curves of acrylic acid/itaconic acid hydrogels in solutions of metal ions were plotted and representative swelling curves are shown in Figure 1. The percentage swelling increases with time but after some time constant percentage swelling is observed. The values of the degree of equilibrium hydration for every metal and concentration studied are given in Table I.

Water diffusion into the hydrogel (swelling) and metal binding to carboxylic groups, which decreases the ionic pressure inside the hydrogel (deswelling), are competitive. At low metal concentrations ($\leq 10^{-4} M$), the metal bound to carboxylic groups is negligible, and swelling is produced by the difference between ionic pressures inside and outside the hydrogel. As the salt concentration increases, the appearance of a complex between metal ions and carboxylic groups is more probable and a simultaneous pH decrease in the outer solution is observed (Table II). The electrostatic

TABLE I
Swelling Parameters of Acrylic Acid/Itaconic Acid Hydrogels in Metal Aqueous Solution

C[M] ²⁺ (M)	H _∞ (%)						
	Cu	Zn	Ni	Co	Cd	Hg	Pb
10 ⁻⁵	1639	2323	2105	2320	1482	1960	1375
10 ⁻⁴	1527	1773	1663	2183	1441	1534	1222
10 ⁻³	1065	1499	1529	1527	1120	803	1143
10 ⁻²	545	1153	1092	1083	818	407	309
10 ⁻¹	233	903	974	922	750	134	302
1	104	477	585	362	671	94	92

reaction will protect against a lower strength and the mobile ion concentration in the external solution will approach that inside the gel. These factors cause the swelling to decrease.

In all examples the pH of the eluted solution was found to be lower than that of the parent solution, suggesting that chelation takes place by competitive mechanisms, one of which may be involved in proton liberation. This is compatible with the fact that the complex formation is accompanied by liberation of hydrogen with a decrease of pH. It should be noted that none of these trends was observed when Hg(NO₃)₂·H₂O or Pb(CH₃COO)₂·3H₂O was used. The Hg²⁺ has a high tendency to generate an equivalent of hydroxyl ions in acidic medium. To prepare solutions of this particular metal we used a diluted solution of HNO₃ to avoid Hg(OH)₂ precipitation, which takes place at pH ≥ 4 for C(Hg)²⁺ = 10⁻⁵ M and pH ≥ 2 for C(Hg)²⁺ = 10⁻¹ M. The difference between the pH of the sample and the pH of the eluent when using Pb²⁺ salts was low, and may account for the acetate buffering effect.

The phenomenon observed in our experiments reveals that the absorbents swelled first and then deswelled while the hydrogels were immersed into high-concentration salt solutions. This event can be explained by the fact that the swelling step corresponds to the water entering the network by the difference in osmotic pressure and the deswelling step is related to the exchange capacities of cations. The dried gel sample, which had once been immersed in the high concentration of cation solution, will never be swelled in water again. This behavior can be attributed to the

increase in the crosslinking density attributed to the complexation of the cation with the carboxylic group. Figures 2 and 3 show some representative results for the deswelling behavior of acrylic acid/itaconic acid hydrogels in different cation salt solutions.

The following equation is used to determined the nature of the diffusion of metallic ions into hydrogels:

$$F = kt^n \quad (3)$$

where F denotes the amount of cation fraction at time t , k is a constant related to the structure of the network, and the exponential n is a number used to determine the type of diffusion.¹⁸ For cylindrical shapes, $n = 0.45-0.50$ corresponds to Fickian diffusion, whereas $0.50 < n < 1.0$ indicates that diffusions are of the non-Fickian type; diffusion and relaxation are isochronally equivalent. Equation (3) is applied to the initial stages of swelling and a plot of $\log F$ versus $\log t$ yields a straight line up to an almost 60% increase in the mass of the hydrogel. For the hydrogel studied, $\log F$ versus $\log t$ was plotted using the kinetics of swelling, some representative results of which are shown in Figure 4. The exponents were calculated from the slope of the lines.

Diffusion coefficients were calculated from the following relation¹⁹:

$$D = \frac{0.049}{(t/4l^2)^{1/2}} \quad (4)$$

where t is the time at which the swelling is one half the equilibrium value and l is the radius of cylindrical

TABLE II
Variation of the pH of an Aqueous Solution in Contact with Acrylic Acid/Itaconic Acid (80/20%) Hydrogels

C(M) ²⁺	Cu		Zn		Ni		Co		Cd		Hg		Pb	
	pH _i	pH _f	pH _i	pH _f	pH _i	pH _f	pH _i	pH _f	pH _i	pH _f	pH _i	pH _f	pH _i	pH _f
10 ⁻⁵	5.76	3.84	6.18	4.26	6.22	4.24	6.28	4.36	6.69	4.36	4.49	3.63	6.63	5.85
10 ⁻⁴	5.67	3.75	6.09	3.60	6.12	3.57	6.17	3.57	6.32	3.76	3.17	3.25	6.28	5.58
10 ⁻³	5.32	3.01	5.58	3.05	6.09	2.86	5.91	2.86	6.13	3.05	2.14	2.48	6.06	5.32
10 ⁻²	4.76	2.65	4.63	2.93	6.03	2.64	5.83	2.52	5.88	2.67	1.00	1.62	5.91	5.16
10 ⁻¹	4.02	2.50	3.30	2.88	5.25	2.61	5.33	2.32	5.42	2.31	0.10	0.81	5.80	5.68
1	3.13	2.28	4.53	2.67	4.68	2.25	4.02	1.91	4.09	1.63	0.07	0.32	5.50	5.14

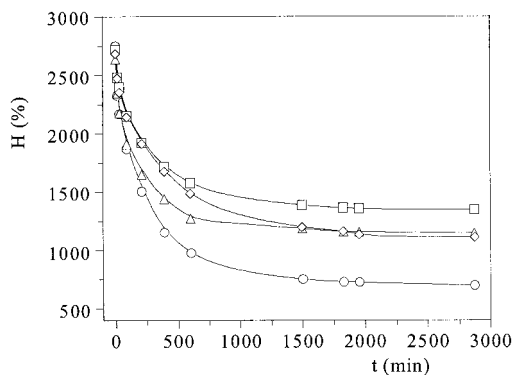


Figure 2 Deswelling behavior of AA/IA (80/20%) hydrogel in the cation aqueous solution at $C(M)^{2+} = 10^{-2} M$: (○) Cu; (□) Zn; (△) Ni; (◇) Co.

polymer sample. The values of diffusion parameters of acrylic acid/itaconic acid hydrogels are listed in Tables III, IV, and V.

The results in Table III indicate that the n values for acrylic acid/itaconic acid copolymeric gels at various concentrations are decreased with increasing concentration. This evidence indicates that the swelling transport mechanism in salt solutions will be transformed from non-Fickian to Fickian transport with increasing concentration. Diffusion of metal ions inside the gel was generally of the non-Fickian type, and values of n were over 0.50. Nevertheless, at high salt concentration (10^{-1} and $1M$), the behavior is different: the n values for some metallic cations were about 0.50 [for $C(M)^{2+} = 10^{-1} M$, $n \approx 0.50$ for Cu, Pb, and Hg; for $C(M)^{2+} = 1M$, $n \approx 0.50$ for Cu, Pb, Hg, and Zn cations], which suggests a Fickian mechanism, and transport of ions is by diffusion. It must be taken into account that at high salt concentration the swelling is poor for all cations with $n \leq 0.50$, where the swelling is maximal at 50% for Cu, Pb, and Hg. For Zn, Ni, Co,

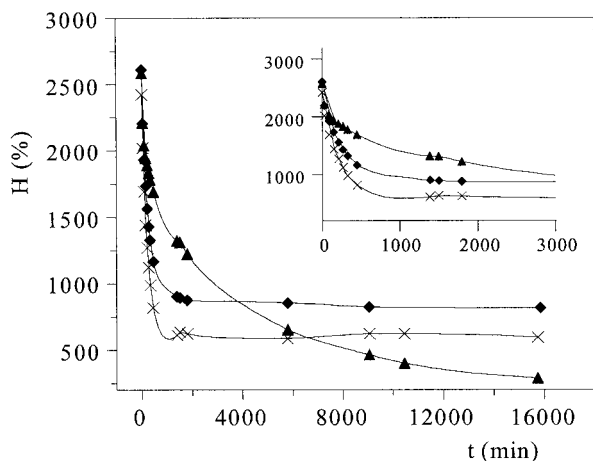


Figure 3 Deswelling behavior of AA/IA (80/20%) hydrogel in the cation aqueous solution at $C(M)^{2+} = 10^{-2} M$: (▲) Hg; (◆) Cd; (×) Pb.

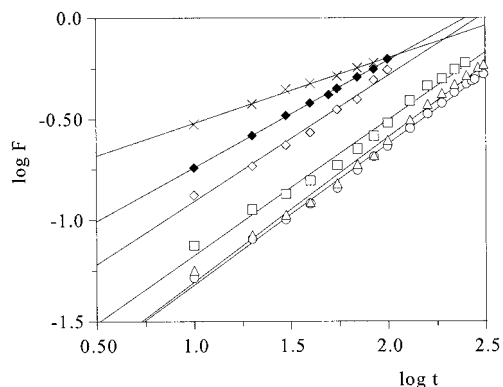


Figure 4 Swelling kinetics curves of AA/IA (80/20%) hydrogels in Cu(II) aqueous solution: (○) $10^{-5} M$; (△) $10^{-4} M$; (□) $10^{-3} M$; (◇) $10^{-2} M$; (◆) $10^{-1} M$; (×) $1M$.

and Cd cations, these values are around 70–90% and the diffusion exponent deviates from 0.50 values. For an anomalous mechanism the coupling between molecular transport and stress relaxation during swelling becomes more pronounced as the deviation, with respect to the Fickian mechanism, increases. Our data also show that the degree of swelling in the lowest concentration is the system that deviates more from Fickian behavior.

On the other hand, experimental values (Tables IV and V) showed that values of the diffusion coefficient D are decreased with an increase of metal ion concentration. The reason for this is the greater degree of swelling at equilibrium in acrylic acid/itaconic acid when the concentration decreases. For a particular cation the diffusion is faster when the degree of swelling is lowest. Both processes are competitive.

pH and concentration effect on the absorption

To investigate the effect of pH on the M^{2+} absorption capacities of the hydrogels, absorption experiments were conducted at various pH values with a fixed temperature ($T = 25^\circ C$). Table VI shows the change in the absorbed M^{2+} ions onto the acrylic acid/itaconic acid hydrogels. Consistent with a polyelectrolyte system, absorption of M^{2+} ions is strongly dependent on the pH. The effect of pH was observed at pH values above 4, which is linked with carboxylic acid dissociation. Decreasing the pH to 2–3 leads to an uncharged gel. Under this condition, the swelling and the absorption trends to very low values.

The study was carried out only for the metal ions that are not susceptible to precipitation at these concentrations and pH values. A retention profile shows the metal ion retention (R) versus pH, $R = \text{metal retained}/M_0$, where M_0 is the initial amount of metal. R is generally expressed as a percentage and is called “the retention capacity of a polymer.” In Figure 5, the

TABLE III
Values of Kinetic Exponent n and Correlation Coefficient for Kinetic Exponent γ of Salt Solution Penetration Through Acrylic Acid/Itaconic Acid (80/20%) Hydrogels

Cation	Log C(M) ²⁺	-5	-4	-3	-2	-1	0
Cu	n	0.71	0.70	0.67	0.62	0.53	0.32
	γ	0.9984	0.9963	0.9939	0.9934	0.9995	0.9980
Zn	n	0.65	0.64	0.61	0.60	0.60	0.56
	γ	0.9958	0.9910	0.9978	0.9982	0.9978	0.9990
Ni	n	0.69	0.68	0.67	0.65	0.62	0.60
	γ	0.9958	0.9993	0.9995	0.9990	0.9995	0.9995
Co	n	0.67	0.64	0.64	0.64	0.63	0.50
	γ	0.9995	0.9996	0.9996	0.9996	0.9998	0.9981
Cd	n	0.67	0.66	0.65	0.64	0.60	0.59
	γ	0.9981	0.9978	0.9984	0.9909	0.9973	0.9972
Pb	n	0.77	0.71	0.61	0.55	0.50	0.43
	γ	0.9966	0.9983	0.9992	0.9978	0.9938	0.9987
Hg	n	0.65	0.61	0.54	0.54	0.51	0.47
	γ	0.9996	0.9996	0.9996	0.9996	0.9995	0.9980

profiles of the retention for the different metal ions studied are shown as a function of pH.

The figure clearly shows a dependency of the retention profile on the initial metal ion concentration. Although the retention capacity percentage decreases with an increase in the metal concentration, the absolute amounts of metal retained increase, as seen in Table VI. For example, at pH = 5, the hydrogel acrylic acid/itaconic acid (80/20%) is able to retain 0.866 mmol (27.5 mg/g_{xerogel}) of Cu(II) when the initial metal amounts are 1 mmol, but retains 2.501 mmol (79.4 mg/g_{xerogel}) when the initial metal amounts are 10 mmol. The gel was not powerful enough to remove the comparatively high concentration of metal ions. Complex formation was dependent on the pH, which also increased with initial concentration of M(II); thus the higher concentration, the higher the metal uptake.

To recover the hydrogel, different concentrations of acid solution (H₂SO₄, HNO₃, and HCl) were added to the cation-loaded gel. Table VII compiles these results. The stripping kinetics is faster than the extraction kinetics, partly as a result of the low swelling of the loaded hydrogel, which decreases the diffusion distances of ions inside the gel. All cations were best eluted in acid medium. In general, increasing the con-

centration of eluant increased the recovery of the hydrogel.

Desorption of copper, nickel, and cobalt was shown by the coloration of the solution and the return of hydrogels to their original colors.

CONCLUSIONS

The absorption of some divalent metal cations in poly-(acrylic acid-itaconic acid) hydrogels from aqueous solution was performed. The pH variation observed in the outer solution shows that extraction proceeds by cation exchange and an acid-base rearrangement of the hydrogels occurs. Metal binding to carboxylate groups leads to gel shrinking attributed to the neutralization of the carboxylate charge by metal complex formation and by protonation. The final degree of swelling in salt solution is closely related to the selectivity of -COO⁻ ion for the cation and to the cation concentration in the solution. The deswelling behavior occurred as the metal ion concentration of the external salt solution increased. The diffusion of metal ions into acrylic acid/itaconic acid hydrogels has non-Fickian

TABLE IV
Diffusion Constant k for Acrylic Acid/Itaconic Acid (80/20%) Hydrogels in Aqueous Salt Solutions

Log C	$k \times 10^2$						
	Cu ²⁺	Zn ²⁺	Ni ²⁺	Co ²⁺	Cd ²⁺	Pb ²⁺	Hg ²⁺
10 ⁻⁵	0.95	1.62	1.19	0.84	1.36	1.04	1.10
10 ⁻⁴	0.96	1.81	1.28	0.88	1.50	1.16	1.46
10 ⁻³	1.43	2.13	1.48	1.24	1.86	1.17	2.59
10 ⁻²	2.95	2.24	1.48	1.61	2.10	3.57	3.67
10 ⁻¹	5.37	3.12	1.67	1.88	2.21	6.54	8.70
0	14.35	4.22	1.78	2.71	2.34	11.64	9.44

TABLE V
Values of the Diffusion Coefficient of Acrylic Acid/Itaconic Acid (80/20%) Hydrogels in Aqueous Salt Solutions

Log C	$D \times 10^5$ (cm ² s ⁻¹)						
	Cu ²⁺	Zn ²⁺	Ni ²⁺	Co ²⁺	Cd ²⁺	Pb ²⁺	Hg ²⁺
10 ⁻⁵	5.92	2.84	2.91	1.78	2.72	3.86	2.18
10 ⁻⁴	5.29	2.71	2.80	1.69	2.66	2.56	1.99
10 ⁻³	3.68	2.69	2.12	1.59	2.24	2.32	1.34
10 ⁻²	2.55	2.32	2.15	1.44	1.99	1.81	1.23
10 ⁻¹	2.00	2.25	1.01	1.30	1.55	0.95	1.04
0	1.87	1.97	0.62	0.54	1.42	0.83	1.04

TABLE VI
Effects of pH and Metal Ion Concentration on Absorption

C[M] ²⁺ (M)	mg M ²⁺ /g _{Xeroger}					
	Cu ²⁺	Zn ²⁺	Ni ²⁺	Co ²⁺	Cd ²⁺	Pb ²⁺
	pH = 4					
10 ⁻⁵	0.20	0.14	0.13	0.12	0.19	0.72
10 ⁻⁴	2.11	1.21	1.05	0.98	2.03	6.26
10 ⁻³	6.76	3.30	2.32	1.99	4.85	21.54
10 ⁻²	17.42	9.11	7.22	6.54	15.21	64.45
10 ⁻¹	141.28	27.86	25.03	23.25	92.00	483.20
	pH = 5					
10 ⁻⁵	0.32	0.26	0.19	0.17	0.31	0.89
10 ⁻⁴	3.15	2.38	1.18	1.16	2.72	7.85
10 ⁻³	27.5	18.50	4.15	4.07	26.12	76.28
10 ⁻²	79.4	57.32	25.09	23.27	76.6	345.3
10 ⁻¹	396.9	233.40	209.17	210.75	321	969.5
	pH = 7					
10 ⁻⁵	0.32	0.32	0.27	0.24	0.41	1.04
10 ⁻⁴	4.65	3.20	1.48	1.50	3.59	10.11
10 ⁻³	31.8	27.30	9.33	9.12	29.75	92.30
10 ⁻²	187.2	158.75	66.21	67.41	168.73	367.61
10 ⁻¹	432.65	320.21	265.25	261.46	392.25	—

character and will be transformed to a Fickian transport mechanism with increasing concentration.

The absorption of cations depended not only on the pH but also on the ion metal concentration. The retention behavior showed that at pH values of 5 and 7 all the metal ions were retained above 60% only at the lowest concentration (10⁻⁵ M), the retention being higher at pH 7 than at pH 5. At high concentration (10⁻¹ M) all cations were retained only under 20%.

Metal stripping from a loaded hydrogel is readily achieved in acid solution. These hydrogels can be used as potential sorbents to remove some cations from wastewater and aqueous effluent.

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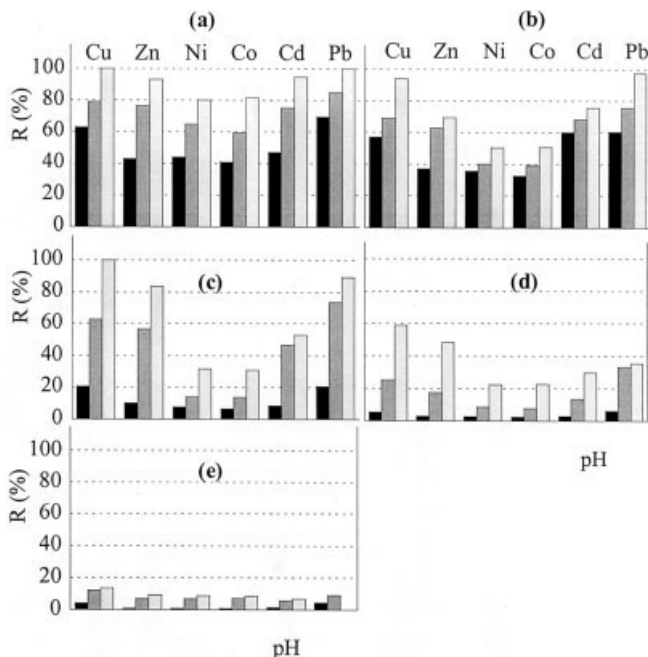


Figure 5 Retention values of metal ions at different pH values: (■) pH 4, (▣) pH 5, (▤) pH 7: (a) 10⁻⁵ M; (b) 10⁻⁴ M; (c) 10⁻³ M; (d) 10⁻² M; (e) 10⁻¹ M.

TABLE VII
Recovery of Metal (%) Ions from Acrylic Acid/Itaconic Acid (80/20%) Hydrogels Loaded with Metal Aqueous Solution, C(M)²⁺ = 10⁻³ M, at 25°C

Cation	0.01 M	0.1 M	1 M
	H ₂ SO ₄ eluent		
Cu	71.5	96.8	100.0
Zn	72.6	89.7	99.7
Ni	65.2	98.4	100.0
Co	67.5	68.3	98.4
Cd	70.2	70.5	95.2
Pb	72.1	77.0	89.7
	HCl eluent		
Cu	70.3	96.0	100.0
Zn	73.5	100.0	99.4
Ni	61.2	99.1	100.0
Co	62.1	71.2	97.5
Cd	63.4	69.7	99.5
Pb	75.2	72.6	88.0
	HNO ₃ eluent		
Cu	64.5	94.8	99.7
Zn	81.6	86.7	100.0
Ni	65.2	95.4	100.0
Co	67.2	78.3	96.3
Cd	71.2	73.4	94.1
Pb	77.8	75.0	86.0

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